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## **EFFECT OF PARAMAGNETIC IRON IONS DOPING ON ELECTRICAL CONDUCTION MECHANISMS OF LAYERED SODIUM LITHIUM TRI TITANATES**

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### **ABSTRACT**

The iron doped layered ceramic samples ( $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7:\text{XFe}$  ( $0.01 \leq X \leq 0.1$ )) have been prepared using high temperature solid state reaction. The room temperature Electron Paramagnetic Resonance investigations exhibit that at lower percentage of doping the substitution of iron ions occur as  $\text{Fe}^{4+}$  at  $\text{Ti}^{4+}$  sites, whereas for higher percentage of doping  $\text{Fe}^{3+}$  ions occupy the two different interlayer Sodium/Lithium alkali sites. In both cases the charge compensation mechanism should operate to maintain the overall charge neutrality of the lattice. The existence of first peak at 523K for all iron doped derivatives in conductivity curves may be due to ferroelectric phase transition. The corresponding  $\ln(\sigma T)$  versus  $1000/T$  plots have been divided into four distinct regions, namely region I, anomalous region, region II and region III. Various Conduction mechanisms have reported during the frequency and temperature range of studies.

**Key Words:** Layered ceramics; Electrical conductivity; Electron Paramagnetic Resonance

### **INTRODUCTION**

Alkali and alkaline earth titanates are used in several applications. [Admas et al. 1996] The alkali metal titanates  $\text{A}_2\text{Ti}_n\text{O}_{2n+1}$  ( $n=3-8$ ,  $A= \text{Na, Li, K}$ ) crystallize in a monoclinic structure. [Feist 1998, Li 1999, Shim 1995] Materials for  $n=3$  or 4 consist of  $(\text{Ti}_3\text{O}_7)^{2-}$  layers held together by alkali-metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ), with a low alkali metal content ( $n=6-8$ ), they show a tunnel structure. The crystal structure of  $\text{Na}_2\text{Ti}_3\text{O}_7$  was solved by Anderson and Wadsley. [Anderson 1961] Recently, the crystal structure of  $\text{Na}_2\text{Ti}_3\text{O}_7$  has been refined by Yakubovich and Kireev. [Yakubovich 2003] Machida et al. [Machida et al. 2003] have reported pillaring and photocatalytic properties of partially substituted layered titanates;  $\text{Na}_2\text{Ti}_{3-x}\text{M}_x\text{O}_7$  and  $\text{K}_2\text{Ti}_{4-x}\text{M}_x\text{O}_9$  ( $M= \text{Mn, Fe, Co, Ni and Cu}$ ). ac conductivity measurements of  $\text{Na}_2\text{Ti}_3\text{O}_7$ ,  $\text{K}_2\text{Ti}_4\text{O}_9$  and their niobium- substituted products have been investigated by Kikkawa et al. [Kikkawa 1985]  $\text{Na}_2\text{Ti}_3\text{O}_7$ ,  $\text{K}_2\text{Ti}_4\text{O}_9$ ,  $\text{K}_{2-x}\text{Rb}_x\text{Ti}_4\text{O}_9$ , and their ( $\text{Na}_2\text{Ti}_3\text{O}_7$  and  $\text{K}_2\text{Ti}_4\text{O}_9$ ) iron and manganese doped derivatives have been investigated through electron paramagnetic resonance (EPR) and dc conductivity measurements by our group. [shripal et al. 1989, 1991, 1991 1992, & Pal et al. 2005, 2007, 2009, 2010, 2010 ] Very recently, Shripal et al. [Shripal et al. 2005, 2005] have further reported the dielectric spectroscopic investigations on pure and manganese doped layered  $\text{Na}_2\text{Ti}_3\text{O}_7$ , and  $\text{K}_2\text{Ti}_4\text{O}_9$  ceramics. Accordingly, it seems to be very interesting to synthesize and characterize  $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$  with 0.01, 0.05 and 0.1 molar percentage of  $\text{Fe}_2\text{O}_3$  doped derivatives denoted as ISLT-1 ISLT-2 and ISLT-3 through Electron Paramagnetic Resonance and ac conductivity investigations.

### **MATERIALS AND METHODS**

The polycrystalline samples of iron (0.01, 0.05 and 0.1 mol%) doped Sodium Lithium Tri Titanates are prepared by adding desired molar percentages of  $\text{Fe}_2\text{O}_3$  (99.7% pure AR grade) powder in the mixture of  $\text{Na}_2\text{CO}_3$  (99.9% pure AR grade),  $\text{Li}_2\text{CO}_3$  (99.9% pure AR grade) and  $\text{TiO}_2$  (99.9% pure AR grade)

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powders, taken in the molar ratio of 1.045:0.055:3.5. The resulting product is heated in air at 1100 K for 16 h, cooled to room temperature (RT), subjected to grinding in acetone to yield fine powder and compressed at 15 MPa using a die to obtain a pellet (size, 10.25 mm diameter and 1.20 mm thickness). The pellet is then covered with powder of the same composition in order to prevent reaction with the crucible and also to ensure minimum soda loss, then sintered in air at 1100 K for 14 h and cooled to room temperature at a rate of 3 K min<sup>-1</sup>. Iso-Debye flex 2002 Richseifert and Co. diffractometer using Cu K $\alpha$  radiation generated at 30 kV and 20 mA has collected XRD patterns for all the compositions. The EPR spectra have been recorded on a Varian E-line Century Series Spectrometer E-109 operating at X-band frequencies (~9.3 GHz). All the spectra were recorded on the sliced pellets of doped derivatives filled in a quartz tube of 6mm outer diameter. To get the first derivative of EPR signals 100 KHz field modulation was used. The magnetic field was calibrated accurately with a Varian E-500 digital nuclear magnetic resonance gauss meter. The Varian temperature controller (E-257/WL-257) was used to maintain the desired sample temperature from 88K to 573K for a sustained length of time with an accuracy of about 0.5K. However the actual temperature of the sample is measured with help of a potentiometer using a copper constantan thermocouple junction at the sample site. Flat faces of pellet are subsequently coated with silver paint and allowed to dry in air. Subsequently, the pellet is mounted in the sample holder (designed for electrical measurements) which, in turn, is evacuated to 10<sup>-3</sup> mbar. The upper part of sample holder is cooled by continuous flow of chilled water. All the dielectric and AC conductivity measurements have been made with impedance analyzer modal HP 4194A using an AC signal of 500 mV superposed. Parallel capacitance ( $C_p$ ) and dielectric loss ( $\tan \delta$ ) are measured from the bulk AC conductivity ( $\sigma_{AC}$ ) values are obtained by using the following expression [B. Tareev 1979]:  $\sigma_{AC} = (t/A) \omega C_p \tan \delta$  Where  $t$  is the thickness, 'A' is area of cross-section of pellet,  $\omega$  is frequency of measurement. Also,  $\omega C_p \tan \delta$  stands for conductance (G).

### RESULTS AND DISCUSSION

The formation of iron doped Sodium Lithium Tri Titanates is confirmed by the XRD-patterns obtained at room temperature (RT) shown in fig. 1(a). XRD patterns for Na<sub>1.9</sub>Li<sub>0.1</sub>Ti<sub>3</sub>O<sub>7</sub> and their all iron-doped derivatives are in very well agreement with those reported in the literature for Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. [Anderson 1961, Yakubovich 2003] Idealized structure of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> and Na<sub>2-x</sub>Li<sub>x</sub>Ti<sub>3</sub>O<sub>7</sub>, where X= 0.1 Edge shared rectangular unit and sphere represent TiO<sub>6</sub> octahedron and Na/Li atom respectively are shown in fig. 1 (b) and fig. 1 (c). X-ray powder diffraction patterns of the iron doped derivatives of pure sodium Lithium Tri Titanates (SLT) containing 0.01, 0.05 and 0.1 molar percentage of Fe<sub>2</sub>O<sub>3</sub> (identified as ISLT-1 ISLT-2 and ISLT-3 respectively) depict a single phase and correspond to monoclinic crystal structure with lattice parameter a=8.571 Å, b=3.804 Å, c=9.135 Å,  $\beta$ =101.57° and space group P2/m, reported in literature. [Anderson 1961, Yakubovich 2003] It consists of (Ti<sub>3</sub>O<sub>7</sub>)<sup>2-</sup> layers formed by joining of blocks of six edge shared TiO<sub>6</sub> octahedral with a common corner. The layers are held together by Na<sup>+</sup> /Li<sup>+</sup> ions placed in two different crystallographic sites [Anderson 1961, Yakubovich 2003]. The substitution of Lithium ions in the interlayer space does not affect the crystal structure of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>. This confirms the presents of small Lithium ions with large Sodium ions in the interlayer space as shown in the fig.1 (c), which indicates that Lithium atoms are accommodated with Sodium atoms in a widely opened interlayer space. The room temperature EPR spectra for samples ISLT 1, ISLT 2 and ISLT 3 are shown in Fig.2. The ISLT 1 sample shows a distinct peak at position A with g ~ 4 in the room temperature EPR spectrum with a weak peak 'B' g~2. However, samples ISLT 2 and ISLT 3 give a two broad peaks spectrum, one composite peak 'A' with g ~ 4 and the other a broad peak 'B' with g ~ 2. The 'B' peak builds up in sample ISLT 2 and is more pronounced than peak 'A' in ISLT 3. The variable temperatures EPR investigation have been carried out on heavily doped derivative ISLT-3 between temperature range 203K to 403K. Fig. 3 shows the corresponding spectra in the heating run to cooling run. In the EPR spectrum of ISLT 2, the quite pronounced composite 'A' peak with g ~ 4 cannot be attributed to the 3d<sup>5</sup> configuration of the iron ions. [Abragam 1990] It seems that iron becomes oxidized to Fe<sup>4+</sup> (attaining the 3d<sup>4</sup> configuration) as it

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substitutes for the host  $Ti^{4+}$  ions. Further, the oxygen neighbors of  $Fe^{4+}$  rearrange creating a tetrahedral field that finally leads to abnormal g- value for the ion. A broad peak 'B' with  $g \sim 2$  can, however be attributed to  $Fe^{3+}$  ions occupying the interlayer alkali ( $Na^+/Li^+$ ) sites. Thus the data, about the relative intensities of peaks 'A' and 'B' in the samples with different doping concentrations of iron, indicate that  $Ti^{4+}$  is the preferred site at very low concentrations and alkali ( $Na^+/Li^+$ ) sites at high concentrations. The temperature variation of the EPR spectrum of heavily doped sample ISLT-3 shows that the intensity of composite 'A' peak decreases and even disappears on heating and a complicated spectrum also with  $g \sim 4$  appears at higher temperatures. This new spectrum cannot be attributed to  $Fe^{3+}$  ions with  $3d^5$  configuration, giving g- value  $\sim 2$ . The heating process from 303 K to 403 K results in the change in the microstructure of iron substituted  $Ti_3O_7^{2-}$  layers with the increase in temperature. The corresponding cooling run plot of EPR spectrum shows the recovery of composite 'A' peak at lower temperatures, showing that the microstructure phase change, noted above, is reversible.

With this knowledge about the occupancy of iron ions in the  $Na_{1.9}Li_{0.1}Ti_3O_7$  lattice, it is easy to discuss the results of AC conductivity studies in samples with different iron concentrations. A broad characterization of AC conductivity plots in to four regions is quite evident and the corresponding results are, accordingly discuss by regions in the following sections.

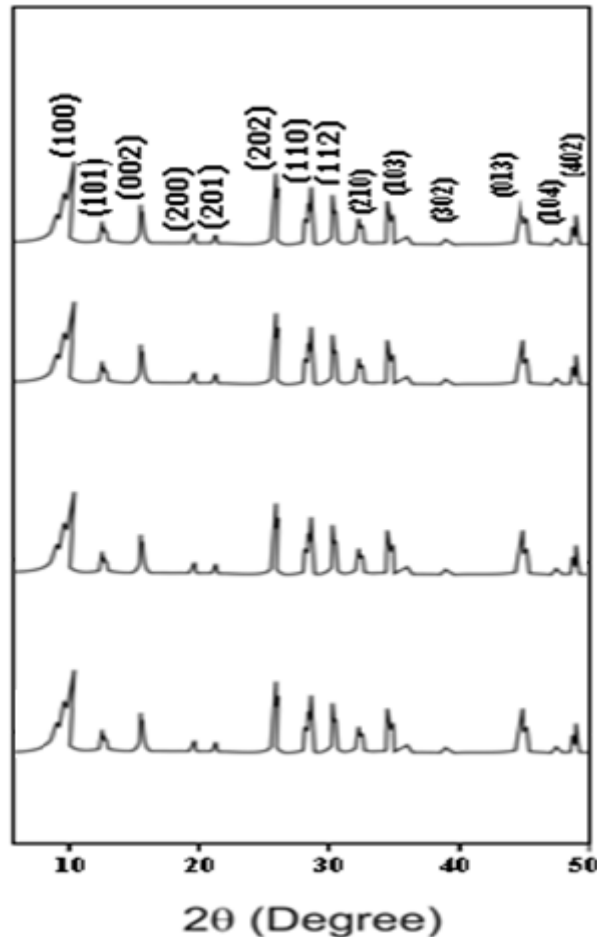
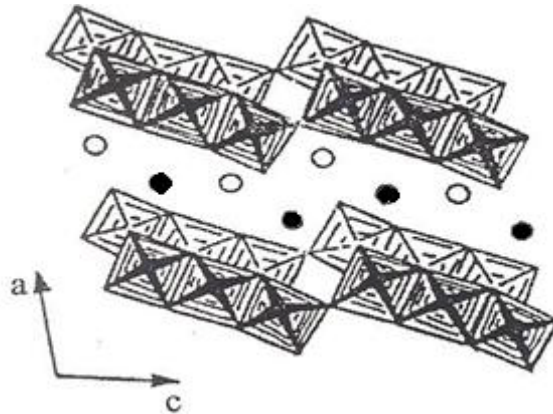
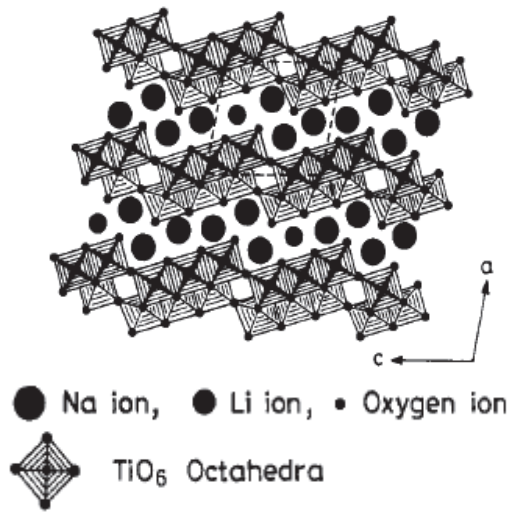


Figure. 1 (a) XRD pattern of iron doped Sodium Lithium Tri Titanates (a) SLT, (b) ISLT-1, (c) ISLT-2, (d) ISLT-3

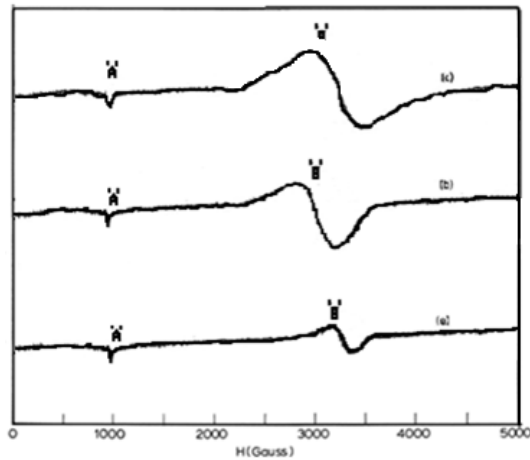
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**Figure. 1(b) Projection along (010) plane of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> structure**

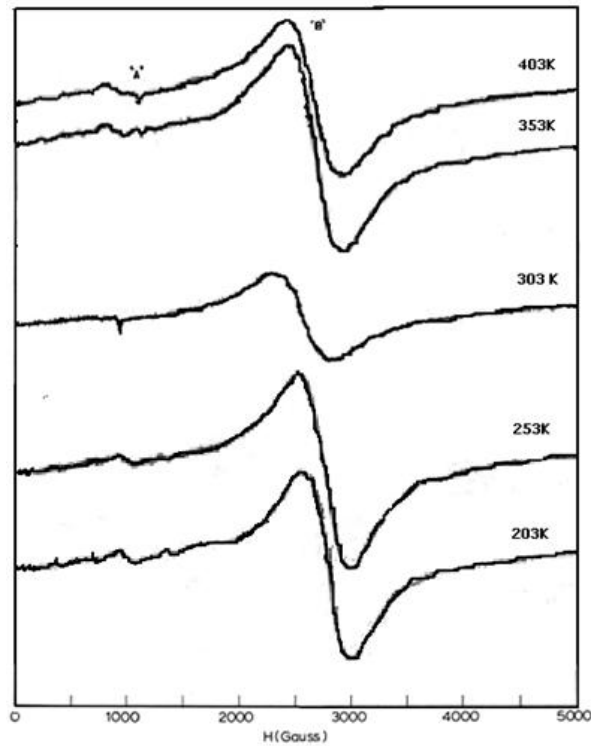


**Figure. 1 (c) Idealized structure of Na<sub>2</sub>-XLiXTi<sub>3</sub>O<sub>7</sub> where X= 0.1 Edge shared rectangular unit and sphere represent TiO<sub>6</sub> octahedron and Na atom respectively**



**Figure 2 EPR spectra of iron doped Na<sub>1.9</sub>Li<sub>0.1</sub>Ti<sub>3</sub>O<sub>7</sub> ceramic (a) ISLT-1, (b) ISLT-2, (c) ISLT-3**

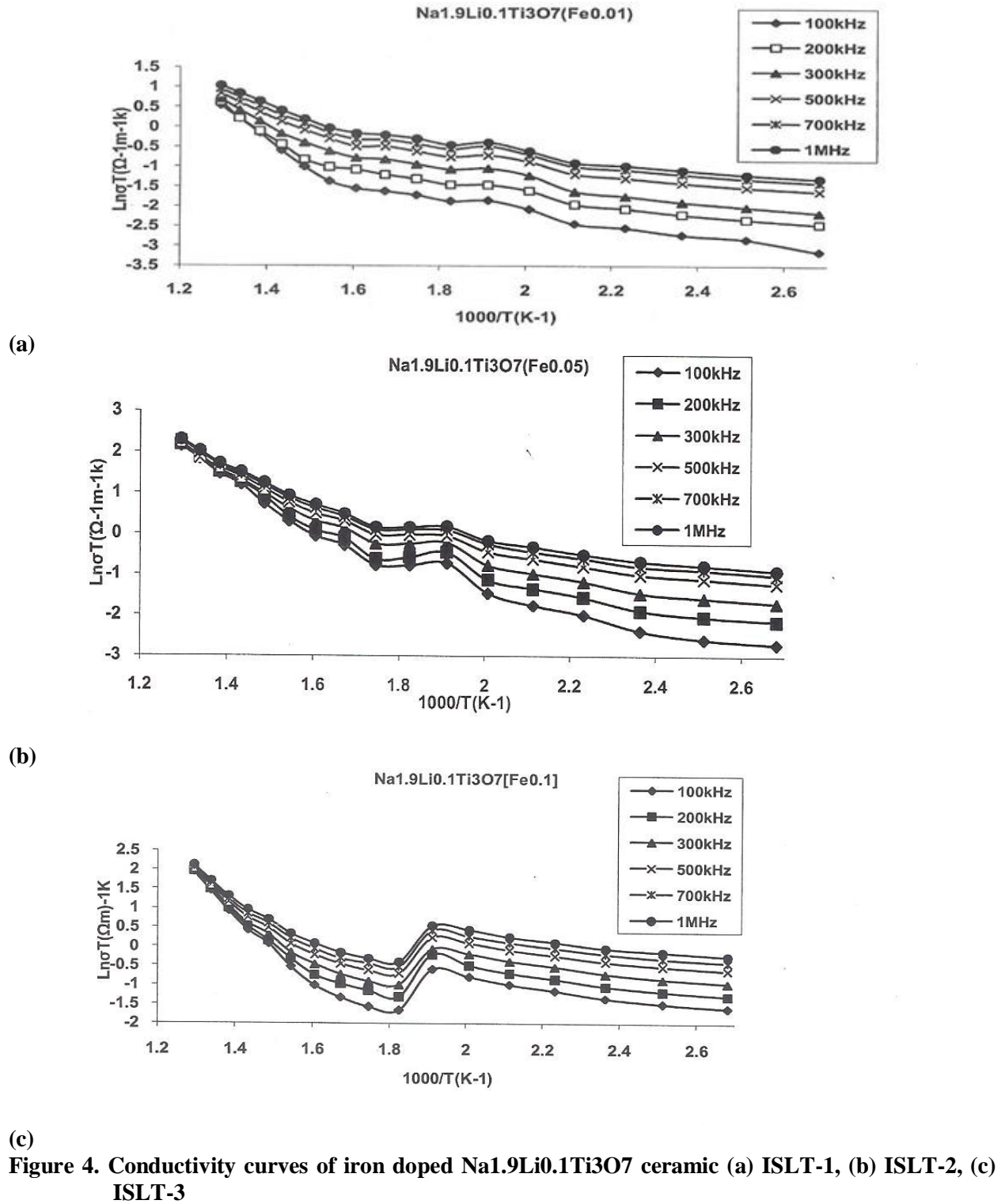
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**Figure 3 Hyperfine spectra of iron doped Na<sub>1.9</sub>Li<sub>0.1</sub>Ti<sub>3</sub>O<sub>7</sub> ceramic ISLT-3**

**Region-I:** The almost frequency dependent and temperature independent region-I exists up to 473K for ISLT-1 and ISLT-2 and 523K for ISLT-3. This nearly temperature independent but strong frequency dependent region may be attributed to the electronic hopping conduction along with the exchangeable inter layer ionic conduction. This behavior of conductivity is similar to that observed by expression  $\sigma(\omega) = A\omega^s$ , where  $s$  is less than unity and the parameter  $A$  is a constant having little dependence on temperature (value being less than unity). Accordingly, the mechanism of conduction involves hopping of electrons between localization sites over shallow barriers with a height distribution along Ti-Ti changes. The higher values of AC conductivity from lower values of DC conductivity as reported in the literature [Maurya 2005] obtained here are due to the contribution of electronic hopping. In ionic host lattices, where the interaction between orbital of neighboring, there is polarization of lattice associated with the presence of electronic carriers and its polarization field referred to as polaron. Two types of polarons play a major role in the conduction process at relatively lower temperature region. When the association is weak (large polarons), conductivity is similar to quasi free electrons which results with small effective mass. When the electronic carrier plus the lattice distortion has the linear dimension smaller than lattice parameter, it is referred to as small polaron and the mobility is strongly affected by the lattice distortion which must move along with the electronic carrier. The loosened electrons from the negative ions and from the impurities in the crystal transported through the solid would contribute to the conduction. The polaron is an electron that always moves around together with the associated lattice polarization that minimizes its energy. The nature of ac conductivity can be interpreted by proposing that electronic hopping conduction, in which the hopping of electrons through shallow barrier along Ti-Ti chain takes part in conduction. These electrons play a major role in this region. Such a frequency dependence of conductivity is attributed to wide distribution of relaxation times due to barrier height. The conduction mechanism for the low temperature region can be expressed by the equation-  $\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}]$

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### Anomalous region

This region exists from 473K to 648K for ISLT-1 from 473K to 573K for ISLT-2 and from 523K to 623K for ISLT-3. The existence of first peak at 523K for ISLT-1 ISLT- 2 and ISLT-3 in conductivity curves may be due to ferroelectric phase transition as reported in literature.[Maurya 2005] It is clear from Fig. (4) that this region is still strong frequency dependent with higher slope for ISLT-1 and less frequency dependent with higher slope for ISLT-2 and ISLT-3 sample. Accordingly, the substitution of iron as  $\text{Fe}^{3+}$  at  $\text{Ti}^{4+}$  sites of sample ISLT-1 encourages trapping of more electrons responsible for electronic hopping conduction in region II as well perhaps, the substitution as  $\text{Fe}^{3+}$  [Pandey 1992] at interlayer  $\text{Na}^+/\text{Li}^+$  sites again furnish configuration of atoms in  $\text{Na}_2\text{Ti}_3\text{O}_7$  lattice in such way that the jumping electrons involved in hopping process diminishes in ISLT-2 and ISLT-3 giving less frequency dependent region as shown in Fig. (4). Furthermore, the higher AC conductivity than DC conductivity values reported earlier [Pandey 1992] can further be explained by proposing that the contribution of electronic hopping conduction increases in the sample ISLT-1. However, the less frequency dependent increase value of conductivity in the ISLT-2 and ISLT-3 in which measure substitution occur as  $\text{Fe}^{3+}$  at interlayer alkali  $\text{Na}^+/\text{Li}^+$  sites can easily be explained by proposing that the associated interlayer ionic conduction is dominated here over electronic hopping conduction. The lowering of limit in this region for iron doped derivatives of SLT this may be understood by proposing that the substitution of  $\text{Fe}^{3+}$  ions in the interlayer space would, in general, the associated with the cation vacancies, would perhaps pull some of the surrounding loose oxygen. [pandey 1992]

**Region II:** The almost temperature dependent and less frequency dependent region exist up 573K to 698K for ISLT-1 and ISLT-2 while from 623K to 698K for ISLT-3. The conduction mechanism of this region found for different iron doped samples, in which the conductivity decrease with rise in temperature, has already been formulated for DC conductivity investigation [23] by proposing that the loose oxygen product by substitution of  $\text{Fe}^{3+}$  at  $\text{Ti}^{4+}$  as explained above will be trapped by the cation vacancies present in the interlayer space leading to decrease in conductivity [23]. In this region too, more frequency dependence for ISLT-1 and less frequency dependence for ISLT-2 and ISLT-3 is seen in the conductivity plots. It suggests that the electronic hopping conduction is still strongly contributing up to this higher temperature region for ISLT-1 which is suppressed in the samples ISLT-2 and ISLT-3 probably due to reduction in the in the population of trapped electrons with the substitution of  $\text{Fe}^{3+}$  at interlayer  $\text{Na}^+/\text{Li}^+$  interlayer alkali sites. Probably, the hindered interlayer ionic conduction and electronic hopping conduction co-exist in this region II.

**Region III:** The almost temperature dependent and frequency independent region III exists from 698K for ISLT-1, ISLT-2 and ISLT-3. The slope of conductivity curves for ISLT-1, ISLT-2 and ISLT-3 are greater than those of region II. It seems that  $\text{Fe}^{4+}$  substitution at  $\text{Ti}^{4+}$  sites loosen off few oxygens from  $\text{Ti}_3\text{O}_7^{2-}$  groups and then participate in conduction in this region. It seems that oxygens making dipoles with  $\text{Ti}^{4+}/\text{Fe}^{4+}$  start to break at the lower limit of this region and then loosen off oxygens to participate in conduction. The ionic conduction in this region involves unassociated vacancies in the interlayer space. Probably in this region the contribution of  $\sigma''(\omega)$  starts to dominate. However I-V dipoles present in the interlayer space has broken up and the mechanism of conduction can now be proposed as unassociated interlayer ionic conduction. The dependence of conductivity on frequency decreases with the increase in temperature for all the compositions. Accordingly, the conduction mechanism in this region may modify interlayer ionic conduction along with the polaronic conduction for ISLT-1, ISLT-2. In ISLT-3 the major substitution occurs as  $\text{Fe}^{3+}$  in the interlayer space (alkali sites) with only little occupancy of  $\text{Fe}^{4+}$  at the  $\text{Ti}^{4+}$  sites. The slope of region III gets decreased. This may be due to the substitution of  $\text{Fe}^{3+}$  in the interlayer space, in general be associated with the cation vacancies, but would become free from their influence up to the lower limit of region III and then perhaps pull some of the loose oxygen obtained due to the reduction of  $\text{Fe}^{4+}$  into  $\text{Fe}^{3+}$  at the  $\text{Ti}^{4+}$  sites. Effect of Fe doping on dielectric response of Na/Li layered ceramics temperature, indicating a decrease in electron hopping conduction and an increase in

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interlayer ionic conduction. This may be due to electronic hopping conduction is dominant at lower temperature and diminishes with the rise in temperature.

### **CONCLUSIONS**

The outcomes of the present investigations may be summarized as iron doped layered Sodium Lithium Tri Titanates ( $\text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7$ ) ceramic with 0.01 0.05 and 0.1 molar percentage of  $\text{Fe}_2\text{O}_3$  doped derivatives can be put in the class of mixed ionic-electronic materials. For lower doping the iron ion occupy  $\text{Ti}^{4+}$  sites as  $3d^4$  configuration  $\text{Fe}^{4+}$  with a  $\text{FeO}_4$  tetrahedral arrangement. For increased doping, the substitution of iron ion occurs as  $\text{Fe}^{3+}$  at interlayer alkali sites (Na/Li sites). The reduction of number of loose electrons from  $\text{Ti}_3\text{O}_7^{2-}$  groups due to substitution of smaller Lithium ions at interlayer  $\text{Na}^+/\text{Li}^+$  sites is seen through conductivity plots of SLT. However iron substitution as  $\text{Fe}^{4+}$  at  $\text{Ti}^{4+}$  sites and  $\text{Fe}^{3+}$  at interlayer alkali ion sites (Na/Li sites), in both cases loosen electrons from  $\text{Ti}_3\text{O}_7^{2-}$  groups participate in conduction through hopping process. Lowest temperature region I is attributed to electronic hopping with exchangeable interlayer ionic conduction, in anomalous region associated interlayer ionic conduction is dominated over electronic hopping conduction. Moreover, the conduction in the region II is due to co-existence of hindered interlayer ionic and suppressed electronic hopping conduction, while conduction in the highest temperature region III is modified interlayer ionic conduction.

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